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During the course of our metalizations a "conditioning" phenomenon was observed whereby higher vapor pressures in the bubbler containing the Cu(hfac)₃ compound were initially observed during a run along with high deposition rates of uniform copper. As bubbling was continued both the vapor pressure and deposition rate steadily decreased and film uniformity became poorer. It is believed that volatile species were outgassing from the bubbler which were responsible for the initial high deposition rate and more uniform films. With prolonged bubbling these components became depleted and the vapor pressure, the deposition rate and film uniformity became diminished. Since the prior art teaches that water vapor can accelerate the deposition of copper from CVD precursors (N. Awaya and Y. Arita, Conf. Proc. ULSI-VII 1992 MRS p345.) it was believed that it could be responsible for the conditioning phenomenon. In the attempts to analyze for H₂O in the Cu(hfac)₃ compound trace H₂O was shown to quickly break down to give a number of products, one of which is Hhfac 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. Hhfac is the protonated "free ligand" of the hfac anion found in all "hfac" compounds. Since Hhfac is known to be an etchant of metal containing surfaces (Norman et al U.S. Pat. No. 5,094,701) and a suppressant of copper deposition from Cu²⁺ (hfac)₃ (W. G. Lai, Y. Xie, and G. L. Griffin, J. Electrochem Soc., Vol. 138, No 11 Nov. 1991) it was an unexpected result to discover its ability to accelerate the deposition of copper from a Cu precursor. Consistent with the above observations it was observed that when stringent precautions were taken to dry all of the equipment in contact with the precursor (and hence eliminate traces of Hhfac), under the same CVD conditions the deposition rate became greatly diminished. The copper films became less specular and nonuniform across the substrate. However, by deliberately adding Hhfac into the CVD chamber when using the precursor under these dry conditions the copper films produced were superior to those achieved when no Hhfac was present.

This

reaction of water with the Cu(hfac)TMVS precursor to give Hhfac was confirmed by adding 50 ppm of H₂O to the pure, dry precursor under oxygen free conditions and showing the resultant presence of Hhfac ligand by gas chromatography/mass spectrometry. In addition solids were observed believed to be a mixture of copper and copper oxide.

A total of 27 runs were made. As shown in FIG. 1 the addition of Hhfac designated by the letter h, Hhfac hydrate designated by the letter H or the vapors of 1,1,1,3,5,5,5-heptafluoro-2,4-pentanedione designated as f7 to the vapors of Cu (hfac)TMVS in a CVD reactor resulted in the deposition rate being increased dramatically. Runs 450 through 467 show clearly the relative increase in the rate of deposition upon the addition of Hhfac to the CupraSelect. Run 468 shows a dramatic increase upon the deposition rate when

f7 is added followed by a reduction of the rate only to 10 .ANG./min upon removal of this additive. The film was also relatively .[.course.]. .ladd.coarse .laddend.and rough in run 469. The addition of **Hhfac** results in an increase in the rate and a return to smoother **films** as indicated by stylus profilometry. Run 471 did not show a large decrease in deposition rate but the film was noticeably rougher than run 470. Addition of **Hhfac** hydrate in run 472 gave a small increase in rate and a smoother **film** than 471. As more Hhfac hydrate was added the rate increased and the increase appeared to be proportional to the amount of Hhfac hydrate added to the reactor.

As shown in FIG. 2 when **Hhfac** (1,1,1,5,5,5-hexafluoro-2,4-pentanedione) was added as a volume percentage of the Cu (hfac)TMVS precursor the deposition rate increased significantly for copper **films** being deposited on platinum, titanium nitride or a gold/chromium alloy substrate. As shown by the seventh data point for deposition on the platinum substrate in FIG. 2 the addition of 7.5 volume percent of Hhfac to the reactor still increased the deposition rate as the Cu(hfac)TMVS source was being depleted.

FIG. 3 shows four copper **films** thickness maps, as determined by the sheet resistivity (blanket areas) and stylus profilometry (patterned areas) of the copper **films** when processed with or without **Hhfac**. All other deposition conditions (wafer temperature 160.degree. C., 40 sccm He carrier gas, precursor temperature 36.degree. C., 500 milli-Torr chamber pressure) for the Hhfac vs. no Hhfac samples were identical. The upper left hand quadrant shows

depositions of copper on a platinum substrate with no addition of Hhfac to the precursor. The resulting film had an average thickness of 2,403 angstrom units with a standard deviation in thickness (.sigma.) of 196 angstrom units or a uniformity of $\pm 14.8\%$. The addition of **Hhfac** to the precursor resulted in the deposition shown in the upper right hand quadrant in FIG. 3 where the copper **film** on the platinum substrate had an average thickness of 4268 angstrom units with a standard deviation (.sigma.) of 103 angstrom units or a uniformity of $\pm 4.1\%$. The lower left and right quadrant samples of FIG. 3 were each given a patterned area of parallel lines of titanium nitride (TiN) deposited on the SiO₂ wafer in the area shown prior to exposure of the patterned substrate to CVD copper deposition. As shown by comparing the two lower quadrants when Hhfac was added to the precursor not only was the copper deposited to a greater depth on the lines, it was also deposited on the unpatterned TiN portion of the substrate. In both the platinum and titanium nitride cases the addition of **Hhfac** increased the copper **film** thickness.

Table 1 indicates how the reflectivity of the copper **films** processed in the presence of added **Hhfac** ligand is consistently higher than those **films** processed in the absence of added **Hhfac** ligand. These reflectance values for copper films are, also controlled by the underlying metal film. That is, smoother base films will result in higher reflectances. For these tests, the base **films for Hhfac** vs. no Hhfac came from the same metallized wafers. The addition of **Hhfac** has improved the reflectance by reducing the surface roughnesses; rougher **films** will have lower reflection coefficients.

	Type	L #	Hits	Search Text	DBs	Time Stamp	C o m m e n t s	E r r o r m e s s a g e s	E r r o r r e c t i o n s
1	BRS	L1	185	(layer or film) with ("methyl iodide" or "CH.sub.3 I" or "CH.sub.2 I.sub.2" or Hhfac or "CH.sub.2 I.sub.2")	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/19 19:26			0
2	BRS	L8	9	1 and damascene	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2003/04/19 19:29			0